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**THIS APPLICATION IS THE ENTRY INTO THE  
NATIONAL PHASE UNDER 35 U.S.C. 371**

**Applicant(s):** DOW GLOBAL TECHNOLOGIES INC.

**International Application No.** PCT/US03/25227

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**Priority Date Claimed:** 12 September 2002

**Title:** PREPARATION OF METAL AMIDE COMPLEXES

**Attorney's Docket No.:** 62398A

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## PREPARATION OF METAL AMIDE COMPLEXES

Cross Reference Statement

5 This application claims the benefit of U.S. Provisional Application No. 60/410,409,  
filed September 12, 2002.

Background of the Invention

10 This invention relates generally to the preparation of certain Group 4 metal amide  
complexes by means of an amine elimination process to produce metal complexes. More  
particularly the present invention relates to a novel process for conversion of initial Group 4  
metal amides to the corresponding metal diamide complexes.

15 The manufacture of Group 4 metal amide complexes has been previously taught in  
US-A-5,312,938, US-A-5,597,935, US-A-5,861,352, US-A-5,880,302, US-A-6,020,444, and  
US-A-6,232,256, and elsewhere. In WO02/38628 Group 4 metal complexes containing  
"spectator ligands" such as amino- substituted cyclic amine compounds were prepared using  
such a process in the first step of a two step process. Suitable amide complexes include Group  
4 metal tetra(N,N-dialkylamido) compounds, especially titanium-, zirconium- or hafnium-  
tetrakis(N,N-dimethylamide) compounds. Suitable alkylating agents include  
trialkylaluminum compounds, especially trimethylaluminum, and alumoxanes.

20 A persistent problem of the foregoing processes is the inability to produce the diamide  
complex in high yield and purity. Because the exchange step is an equilibrium process,  
complete conversion generally cannot be attained even after resorting to the use of elevated  
temperatures and/or venting or vacuum removal of amine byproducts. A process in which  
complexation of the metal by a ligand is facilitated, thereby resulting in the use of lower  
25 reaction temperatures, shorter reaction times, and/or characterized by higher yields, is still  
desired.

Summary of the Invention

30 In accordance with this invention there is provided an improved process for the  
preparation of Group 4 metal amide complexes comprising a monovalent or divalent Lewis  
base ligand the steps of the process comprising contacting a Group 4 metal amide with a  
neutral source of a monovalent or divalent, Lewis base ligand group and a solid, Lewis acid  
under amine elimination conditions to form a Group 4 metal amide complex containing at  
least one less initial amide group per metal moiety than the original Group 4 metal amide, and  
35 recovering the resulting metal complex.

The products are highly valuable for use as catalysts in combination with activating cocatalysts such as alumoxanes or cation forming agents in the polymerization of olefins to high molecular weight polymers.

## 5 Detailed Description of the Invention

All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1999. Also, any references to a Group or Groups shall be to the Groups or Groups reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. For purposes of United States patent practice, the contents of any patent, patent application or publication referenced  
10 herein are hereby incorporated by reference in their entirety, especially with respect to the disclosure of synthetic techniques and general knowledge in the art. The term "comprising" when used herein with respect to a composition, mixture or process is not intended to exclude the additional presence of any other compound, component or step.

15 Suitable Group 4 metal amides for use in the present invention correspond to the formula,  $M(NR_2)_mX_n$ ,

wherein M is a Group 4 metal, especially hafnium;

R independently in each occurrence is a  $C_{1-20}$  hydrocarbyl group, a  $C_{1-20}$  halohydrocarbyl group, or two R groups are joined together thereby forming a divalent  
20 derivative, preferably R, each occurrence is  $C_{1-4}$  alkyl;

X is an anionic ligand other than an amide group of up to 20 atoms not counting hydrogen or two X groups are joined together thereby forming a divalent derivative, preferably each X group is hydride, halide, or a hydrocarbyl-, silyl-, hydrocarbyloxy- or siloxy- group of up to 10 atoms; most preferably chloride or methyl;

25 m is an integer from 1 to 4 and n is an integer equal to 4-m.

Preferred Group 4 metal amides are Group 4 metal tetrakis(N,N-dihydrocarbyl)-amides, especially Group 4 metal tetrakis(N,N-dimethyl)amides, most especially hafnium tetrakis(N,N-dimethyl)amide.

The foregoing Group 4 metal amides are contacted with a neutral source of the desired  
30 Lewis base ligating species thereby generating free amine. Suitable ligand sources are monovalent and divalent compounds of the formula L-H or H-L-H wherein L is a monovalent or divalent Lewis base ligand, in which case the resulting free amine corresponds to the formula  $NHR_2$ . Examples of suitable Lewis base ligating species sources include aliphatic and aromatic diamine compounds, and hydrocarbylamine substituted aromatic heterocyclic  
35 compounds.

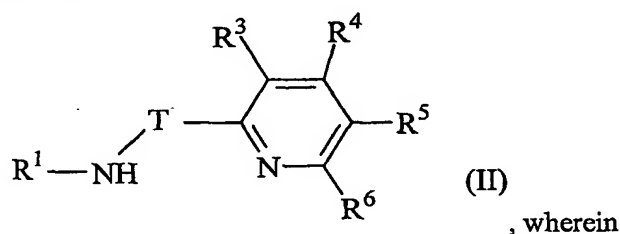
In particular, suitable sources of Lewis base ligating species include difunctional Lewis base compounds disclosed in WO 02/38628, especially hydrocarbylamine substituted heteroaryl compounds of the formula  $R^1HN-T-R^2$  (I), wherein

$R^1$  is selected from alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl, and inertly substituted derivatives thereof containing from 1 to 30 atoms not counting hydrogen;

$T$  is a divalent bridging group of from 1 to 20 atoms other than hydrogen, preferably a mono- or di-  $C_{1-20}$  hydrocarbyl substituted methylene or silane group, and

$R^2$  is a  $C_{6-20}$  heteroaryl group, especially a pyridin-2-yl- or substituted pyridin-2-yl group.

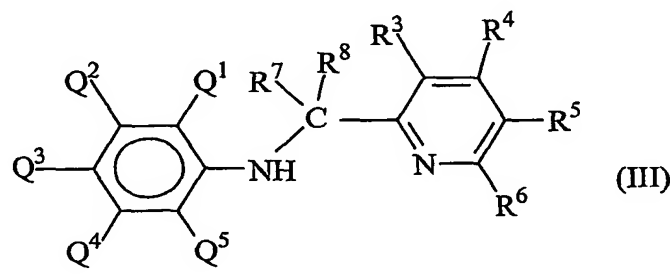
Preferred examples of the foregoing difunctional Lewis base compounds correspond to the formula:



$R^1$  and  $T$  are as previously defined, and

$R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are hydrogen, halo, or an alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl, or silyl group of up to 20 atoms not counting hydrogen, or adjacent  $R^3$ ,  $R^4$ ,  $R^5$  or  $R^6$  groups may be joined together thereby forming fused ring derivatives.

Highly preferred examples of the foregoing difunctional Lewis base compounds correspond to the formula:

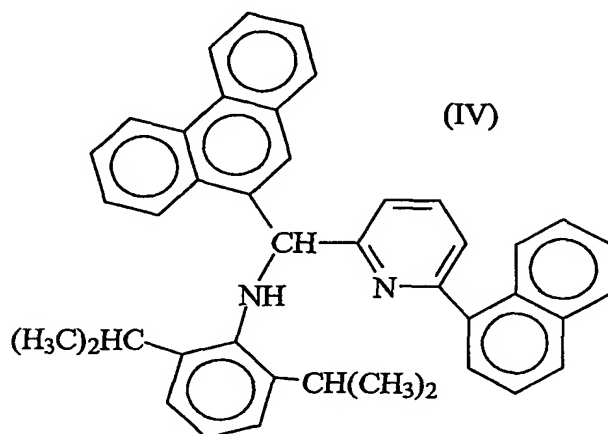


$R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are as previously defined, preferably  $R^3$ ,  $R^4$ , and  $R^5$  are hydrogen, or  $C_{1-4}$  alkyl, and  $R^6$  is  $C_{6-20}$  aryl, most preferably naphthyl;

$Q^1$ ,  $Q^2$ ,  $Q^3$ ,  $Q^4$ , and  $Q^5$  are independently each occurrence hydrogen or  $C_{1-4}$  alkyl, most preferably  $Q^1$  and  $Q^5$  are isopropyl and  $Q^2$ ,  $Q^3$  and  $Q^4$  are hydrogen; and

$R^7$  and  $R^8$  independently each occurrence are hydrogen or a  $C_{1-20}$  alkyl or aryl group, most preferably one of  $R^7$  and  $R^8$  is hydrogen and the other is a  $C_{6-20}$  aryl group, especially a fused polycyclic aryl group, most preferably an anthracenyl group.

The most highly preferred difunctional Lewis base compound for use herein corresponds to the formula:

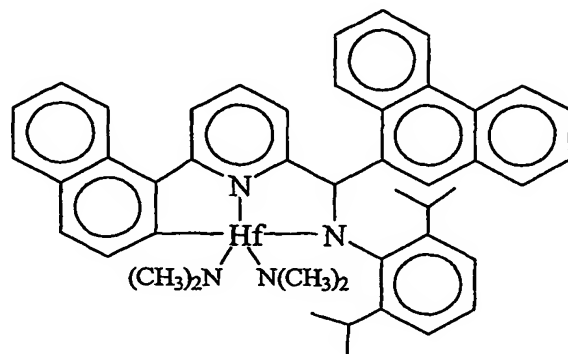


Under the reaction conditions of the present invention, it has been discovered that the hydrogen of the 2-position of the naphthyl group substituted at the 6-position of the pyridinyl group is subject to elimination, thereby uniquely forming metal complexes wherein the metal is covalently bonded to both the resulting internal amide group and to the 2-position of the naphthyl group, as well as stabilized by coordination to the pyridinyl nitrogen atom through the electron pair thereof. Accordingly, preferred metal complexes contain 2 less amide groups than the original Group 4 metal amide reagent and a difunctional Lewis base ligand additionally coordinated to the metal by means of an electron pair.

The foregoing reaction is performed in the presence of the solid Lewis acid. Examples of suitable solid Lewis acids included silica, alumina, clay, aluminosilicates, and borosilicates, preferably alumina. Such reagent uniquely promotes amine elimination by acting as an acceptor or scavenger for the amine. In a preferred embodiment, the scavenger is accessible to volatile amine by-products but the remainder of the reaction mixture does not contact the Lewis acid scavenger. As one example, the Lewis acid may be retained in a column or vessel in operative communication with the headspace of the reactor and the amide groups of the Group 4 metal amide are N,N-dimethylamide groups that form the highly volatile amine, N,N-dimethylamine.

According to the process, the Group 4 metal amide and Lewis base compounds are employed in approximately stoichiometric amounts, preferably in molar ratios (based on amide compound to Lewis base compound) from 1:2 to 2:1. The quantity of solid Lewis acid compound used is preferably from 2:1 to 10 to 1, more preferably from 4:1 to 6:1 based on Group 4 metal amide compound.

As an illustration, starting from hafnium tetrakis(dimethylamide) and excess alumina scavenger, the resulting metal complex prepared according to the present invention in high yield and efficiency is:



The amide elimination conditions used in the present process include moderate temperatures from 0 to 100 °C, especially from 25 to 75 °C, reduced, atmospheric or elevated pressures from 0 to 100 kPa, preferably atmospheric pressure, times from 1 minute to 10 days, preferably from 10 minutes to 2 hours, and use of an aliphatic or aromatic solvent, preferably toluene or ethylbenzene. The resulting complexes may be recovered by filtration, extraction, precipitation, or other suitable technique.

The resulting Group 4 metal complexes are activated to form the actual catalyst composition by combination with a cocatalyst, preferably an aluminoxane, a cation forming cocatalyst, or a combination thereof and desirably employed to polymerize olefins or combinations of olefins, especially ethylene, propylene, 1-butene, 1-hexene, 1-octene and mixtures thereof; mixtures of the foregoing monomers with vinylaromatic monomers or conjugated or non-conjugated dienes; and mixtures of all of the foregoing monomers. The process is characterized by low temperatures and pressures, typically from 25 to 50 °C and pressures from atmospheric to 10 MPa.

Suitable alumoxanes for use herein include polymeric or oligomeric alumoxanes, especially methylalumoxane, triisobutyl aluminum modified methylalumoxane, or isobutylalumoxane; neutral Lewis acid modified polymeric or oligomeric alumoxanes, such as the foregoing alkylalumoxanes modified by addition of a C<sub>1-30</sub> hydrocarbyl substituted Group 13 compound, especially a tri(hydrocarbyl)aluminum- or tri(hydrocarbyl)boron compound, or a halogenated (including perhalogenated) derivative thereof, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, more especially a perfluorinated tri(aryl)boron compound or a perfluorinated tri(aryl)aluminum compound.

The Group 4 metal complexes may also be rendered catalytically active by combination with a cation forming cocatalyst, such as those previously known in the art for use with Group 4 metal olefin polymerization complexes. Suitable cation forming cocatalysts

for use herein include neutral Lewis acids, such as C<sub>1-30</sub> hydrocarbyl substituted Group 13 compounds, especially tri(hydrocarbyl)aluminum- or tri(hydrocarbyl)boron compounds and halogenated (including perhalogenated) derivatives thereof, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, more especially perfluorinated tri(aryl)boron compounds, and most especially tris(pentafluorophenyl)borane; nonpolymeric, compatible, noncoordinating, ion forming compounds (including the use of such compounds under oxidizing conditions), especially the use of ammonium-, phosphonium-, oxonium-, carbonium-, silylium- or sulfonium- salts of compatible, noncoordinating anions, or ferrocenium-, lead- or silver salts of compatible, noncoordinating anions; and combinations of the foregoing cation forming cocatalysts and techniques. The foregoing activating cocatalysts and activating techniques have been previously taught with respect to different metal complexes for olefin polymerizations in the following references: EP-A-277,003, US-A-5,153,157, US-A-5,064,802, US-A-5,321,106, US-A-5,721,185, US-A-5,350,723, US-A-5,425,872, US-A-5,625,087, US-A-5,883,204, US-A-5,919,983, US-A-5,783,512, WO 99/15534, WO99/42467, (equivalent to USSN 09/251,664, filed February 17, 1999).

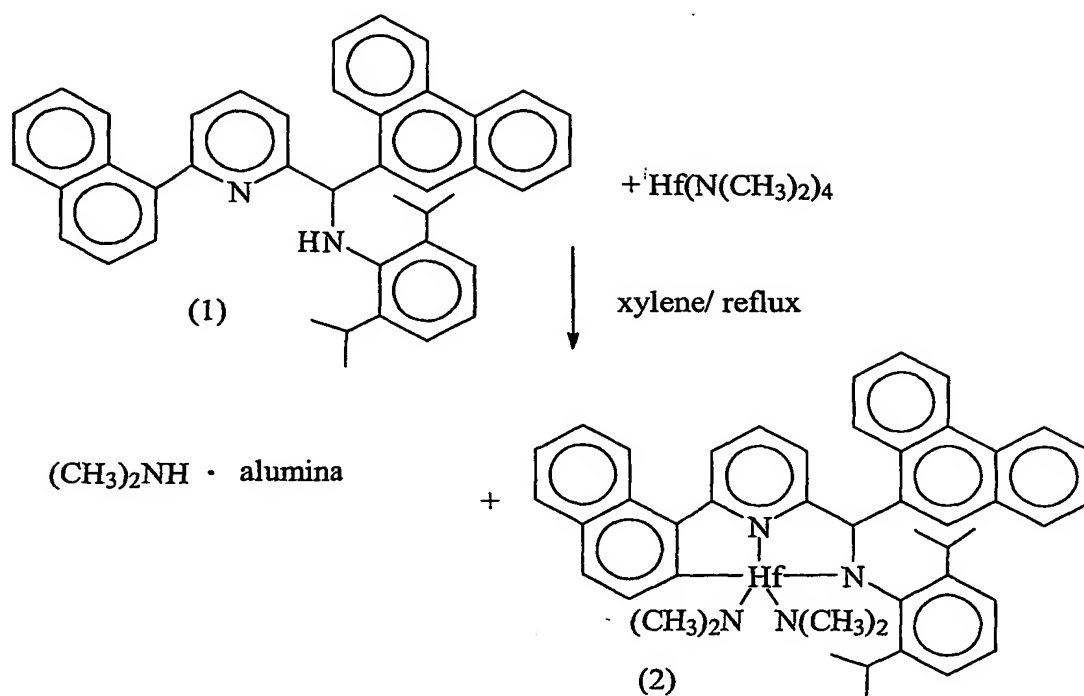
#### EXAMPLES

The skilled artisan will appreciate that the invention disclosed herein may be practiced in the absence of any component which has not been specifically disclosed. The following examples are provided as further illustration of the invention and are not to be construed as limiting. Unless stated to the contrary all parts and percentages are expressed on a weight basis. The term "overnight", if used, refers to a time of approximately 16-18 hours, the term "room temperature", refers to a temperature of about 20-25 °C, and the term "mixed alkanes" refers to a commercially obtained mixture of C<sub>6-9</sub> aliphatic hydrocarbons available under the trade designation Isopar E<sup>®</sup>, from Exxon Chemicals Inc. In the event the name of a compound herein does not conform to the structural representation thereof, the structural representation shall control.

The synthesis of all metal complexes and the preparation of all screening experiments were carried out in a dry nitrogen atmosphere using dry box techniques. All solvents used were HPLC grade and were dried and deoxygenated before their use.

#### Example 1

A metal complex was prepared according to the following reaction scheme:



To a flask fitted with a condenser column packed with dried alumina in a glovebox was added 100 ml of xylene and 16.25 g (0.029 mol) of (1). Hafnium tetrakis(dimethylamide) (12.12 g, 0.034 mol) suspended in 20 ml xylene was added. The resulting suspension was heated to reflux and maintained in that condition for 4 hours. The mixture was then devolatilized leaving 34 g of crude product. To this material 50 g of pentane was added and stirred overnight. The resulting mixture was filtered and the solids washed twice with 12 ml of pentane. The resulting solid was dried under dynamic vacuum yielding 21.3 g of the desired diamide complex as a pale yellow solid.

Catalytic activity was confirmed by polymerization of 450 g of propylene monomer in 500 ml hexane in a 2 L polymerization reactor at 90 °C using 1.0  $\mu\text{mole}$  of catalyst and a hexane solution of methyl-di(octadecylammonium) tetrakis(pentafluorophenyl)borate cocatalyst in 1:1 B:Hf molar ratio.